THE HEAT OF WETTING OF ACTIVATED SILICA GEL

By

George Taylor Bauer

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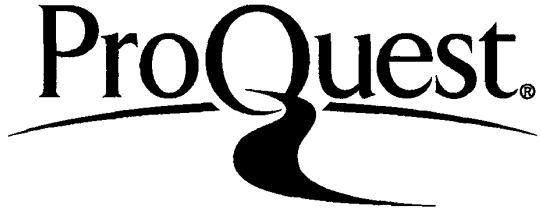

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The structure of silica gel has been rather definitely shown by Fells and Firth (J.Phys.Chem.,29, 241 (1925)), and Jones (J.Phys.Chem.,29, 327(1925)) to consist of capillary pores creating an enormous surface and internal volume and giving to a gel the ability of sorption (adsorption and absorption). As this large surface has associated with it a great amount of energy, destruction of this surface by water will give a heat effect whether it is done by water vapor or water liquid. To partially destroy this surface in steps and to measure the remaining surface energy was the purpose of this work.

As a means of partially destroying the surface of the gel its water content was varied by either adding or removing water from it. This variable water was assumed to be evenly distributed over the surface as regards the lowering of surface energy. The surface of the gel can have active points or centers which under the above assumption would be covered by a deeper layer of water than the less active centers. This would allow a surface to result having a uniformly exposed surface energy or vapor pressure. To allow distillation from points of higher vapor pressure to those of lower vapor pressure

and to allow this condition to reach equilibrium with itself and with the vapor in which it is placed requires time and absence of interfering agencies such as air and changing temperature.

The regulation of the water vapor pressure in a closed system by the use of sulfuric acid solution as the controlled source of water vapor was used in the experiments of Zsigmondy, Bachmann and Stevenson (Z.anorg. Chem.,75,189(1912)), van Bemmelen (Z.anorg. Chem.,30,265(1902)), and Andersen (Z.physik.Chem., 88, 191(1914)) in their work on silicic acid gels. These investigators determined a curve for the adsorption and desorption of water vapor by fresh silica gel and found a hysteresis effect. Patrick and McGavack (J.Am.Chem.Soc.,42, 946(1920)) observed no hysteresis in their investigations of the adsorption of sulfur dioxide on silica gel and ascribed hysteresis effect to the presence of air. Later, Patrick (Colloid Sym. Mono.,7,129 (1929)) observed no hysteresis in the adsorption and desorption curves for water vapor on silica gel. Ray and Ganguly (Faraday Soc.,30, 997(1934)) found a hysteresis effect with water vapor on gel in their experiments carried out at high vacuum.

Lamb and Coolidge (J.Am.Chem.Soc.,42,1146(1920)) and Harkins and Ewing (J.Am.Chem.soc.,43,1787(1921)) expressed the opinion that vapors adsorbed on an adsorbent were held there under an enormous pressure. Lamb and Coolidge calculated that the heat developed in excess of the heat of condensation

was due to compression. Harkins and Ewing indicated that the surface energy of an adsorbent is the seat of great energy and calculated a value of over 20000 atmospheres pressure holding adsorbed molecules on a surface of carbon. Coolidge (J.am.Chem.Soc.,48,1795(1926)) later decided that his high value for compression was too high and instead of stating that net heat of adsorption was due to compression decided on a correlation with Polanyi's theory and destruction of surface. Patrick and Grimm (j.Am.Chem.Soc.,43,2144(1921) calculated the area exposed by 1 g. of silica gel from heat of wetting measurements on the theory that the gel exhibited a water surface and the heat evolved developed from destruction of the total surface energy of this water surface. Patrick and Greider (J.Phys.Chem.,29,1031 (1925)) determined the heat of wetting of silica gel by water vapor at saturation at 0°C. and results obtained were in agreement with the calculations of total surface energy yielding the net heat of adsorption. There appears to be enough agreement between net heat of adsorption and heat of wetting to indicate that the two are the same phenomena. In this case the Lamb and Coolidge empirical equation of $H = KX^{1/n}$ should apply to heats of adsorption calculated from heats of wetting data and heats of condensation.

Three common workable equations for indicating adsorption by a straight line on a log-log graph are: the well known Freundlich Adsorption Isotherm Equation of $X/M = KP^{1/n}$;

Patrick's Capillary Condensation Equation somewhat equivalent to Freundlich's of $V/M = K(Ps/Po)^{1/n}$; and Gregg's adaptation of Patrick's Capillary Condensation Equation of $V/M = K(P/P^oT)^{1/n}$.

Three widely accepted theories of adsorption are namely Langmuir's monomolecular layer adsorption, Zsigmondy's capillary condensation, and Polanyi's multimolecular layer adsorption. Langmuir states that his theory is inaccurate when dealing with porous bodies and application of Zsigmondy's theory is limited. It is doubtful whether with our present knowledge the above theories can be correctly applied but with some of the data given in this experiment a new theory which combines the three preceding ones and that theory which predicts a layer of molecules five or six deep necessary to completely wet a surface (Chamberlain, Phys. Rev., 31, 170, (1920)) is postulated.

EXPERIMENTAL

Apparatus.- The electrically calibrated adiabatic calorimeter including its assessories incorporated most of the features of calorimeters of previous investigators (Williams & Daniels, J. Am. Chem. Soc., 46,903 (1924)), (Ewing & Callaborators, J. Am. Chem. Soc., 54,1335 (1932)) and (W.P. White, J.Am. Chem. Soc. 36, 2292 (1914)). The assessories included a nichrom heating element with heavy copper lead wires, a twenty-four couple copper-constantan thermopile, a five degree Beckmann thermometer, a metallic four paddle blade stirrer with a glass shaft, and an especially designed support for the bulbs.

The nichrom heating element was five centimeters in length welded and soldered to two heavy copper lead wires which were coated with an insulating shellac. The thermopile, connected to a Leeds and Northrup wall type galvanometer sensitivity .014 microampere, indicated temperature differences between the inner calorimeter and outer bath. The thermocouples were each welded and then insulated with a thin coating of special shellac. The support for the bulbs was a very light metallic cradle with a sharpened screw for breaking them and the whole assembly held in the calorimeter by a glass tube through which a glass rod operated as a means of tightening or loosening the screw.

Two beckmann thermometers, one inserted in the inner silvered calorimeter and one in the outer copper sulfate bath were read by an adjustable eye piece clamped to their stems.

The inner and outer stirrers for the inner calorimeter cup and copper sulfate solution respectively were powered by an A.C. 1250 r.p.m. motor. The relative speeds of the two stirrers could be regulated by means of adjustable pulley wheels.

The calorimeter cup was turned out of a brass block giving walls .7mm. thick and was silver plated to insure against corrosion. This silvered cup was 1 cm. from the brass container which with its ground brass cover was completely submerged in a copper sulfate bath. There was at least 7 cm.

of copper sulfate solution surrounding this brass container. For entry into the silvered cup the ground brass cover included five brass chimneys 15 cm. in length.

For preventing heat transfer from the inner calorimeter to the copper sulfate bath a 110 v. alternating current was passed directly through the copper sulfate solution using its container as one electrode and a perforated insulated copper shield around the brass container as the other electrode. A stirrer in the copper sulfate bath eliminated the danger of localized heating and a water cooled copper coil lowered the temperature of the bath when desired. This assembly was then placed in an air bath (Hendricks and Steinback, J.Phys.Chem., 36,1279(1932)) at 25°C. constant to±.02°C. The cabinet for the air bath was equipped with the usual devises for constancy including a mercury thermoregulator, a dry cell relay, an air fan with motor, a nichrom wire heating element #32 5 cm. long, and a water cooled copper coil and bank for cooling.

For measuring the energy of the direct current, which was supplied by two 6 v. batteries connected in parallel, used in equilibrating the heat equivalent of the calorimeter the following pieces of equipment were used: Type 'K' potentiometer, Leeds and Northrup galvanometer, Standard Weston Cell #56567 of 1.0186 v., 0-6 D.C. ammeter, and a Leeds and northrup Standard resistance of .1 ohm and 15 amps.

Material.- Special research silica gel from the Silica

Gel Corporation, Baltimore, Maryland, was satisfactory as a substance of rather definite surface structure and high purity. The gel as received was sorted to first pass a 3 mm. sieve and be retained by a 2 mm. sieve. All discolored, crumbly and opalescent particles were separated from the clear transparent ones over a black surface and discarded.

The water used for the heat of wetting determinations was low conductivity grade. The sulfuric acid and phosphorous pentoxide were both of C.P. quality.

Procedure.- Three different methods for preparing silica gel with a definite water content were followed in this investigation. First, following a procedure of van Bemmelen's, the gel was suspended in vacuum (as regards air) in an atmosphere of water vapor from a sulfuric acid solution. The pressure of the water vapor varied inversely as the concentration of the acid solution and directly as its temperature.

Second, replacing the sulfuric acid with phosphorus pentoxide and using an electric heating element around the gel, the temperature and water vapor pressure of the gel could then be increased with heat while the phosphorus pentoxide retained at 25°C. its original vapor pressure.

Third, in a vacuum apparatus built in this laboratory the gel was heated to various temperatures and evacuation of the liberated water vapor was carried on to a pressure of .0001 mm. of mercury.

By these three methods it was possible to prepare gel with water contents from 36.2% to 1.4% and reproduce these gels at will. In the first method the fact that the vapor pressure of an atmosphere can be controlled by using sulfuric acid solutions was utilized. Using approximately 2.5 g. of gel as received and working in quadruplicate through eleven different atmospheres of controlled vapor pressure spaced from zero mm. to saturation through four temperature ranges the graph, fig I, was obtained. These adsorption-desorption reversible curves indicating no hysteresis could be duplicated and were duplicated three years later which might indicate that the gel did not deteriorate upon standing.

The gel in weighing bottles was suspended in vacuum as regards air over a definite percent by weight of sulfuric acid solution. An ordinary stock bottle was used and the top sealed with a rubber stopper and paraffin. The whole was then submerged in a constant water (oil for the two higher temperatures) bath and allowed to remain for four days. Three days were found sufficient in some of the cases. At the end of this time the gel had adsorbed sufficient water from the vapor to give a weight which was constant at that vapor pressure and temperature. Its own vapor pressure under those conditions was then at equilibrium with that of the acid solution over which the gel was suspended and the water on the gel was evenly distributed over the surface of the gel as regards total surface energy exposed.

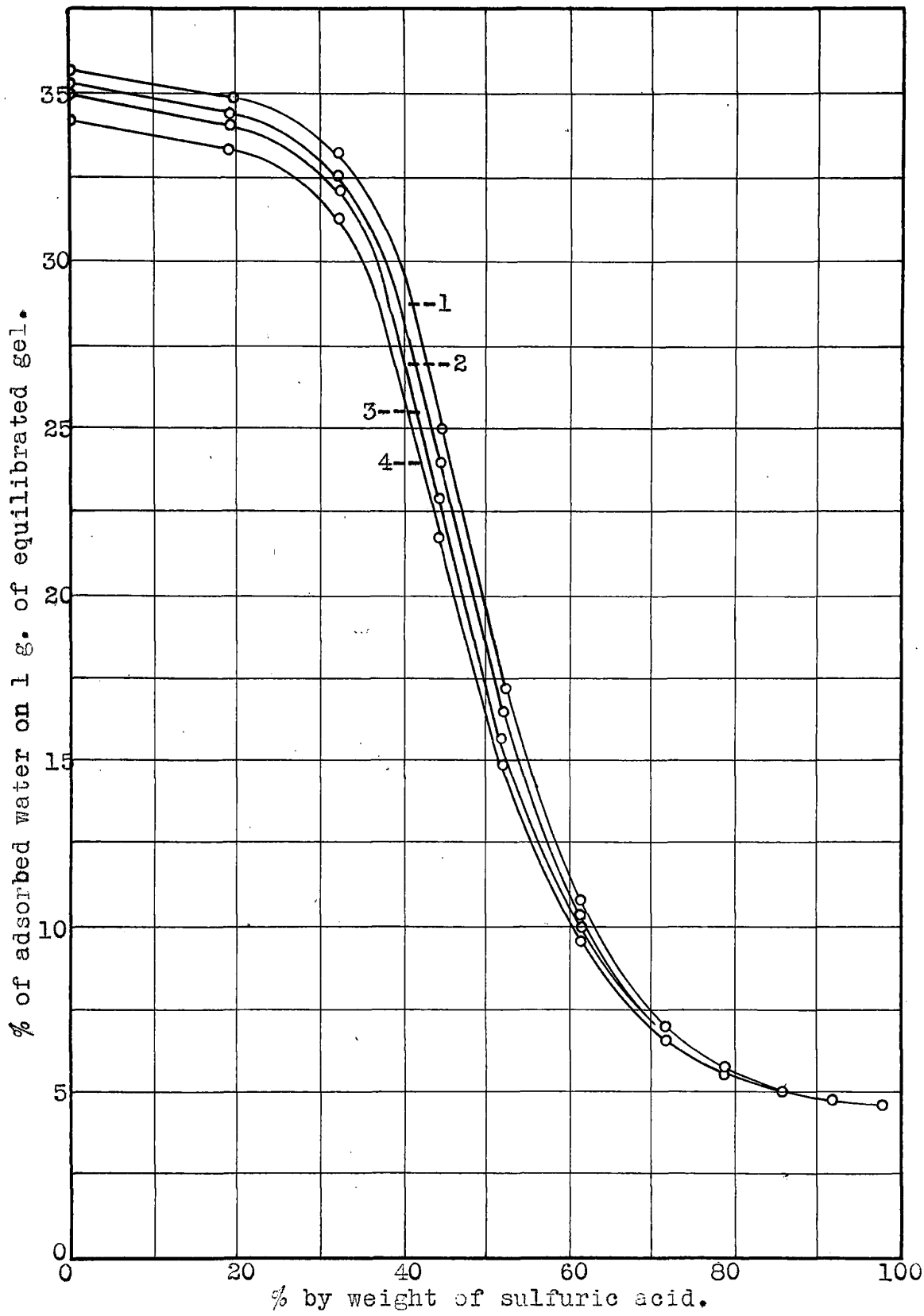

Fig. 1.- Adsorption isotherms: No. 1, 15°C.; No. 2, 25°C.; No. 3, 40°C.; No. 4, 60°C.

By this method gels could be reproduced at any desired water content between the limits of 4.6% to 36.2%. No matter what the water content of the gel as received this method gave expected results within its range.

The second method of varying the gel water content was by means of heating the gel in vacuum over phosphorous Pentoxide the latter held at 25°C. The result was to drive off more water from the gel by increasing its water vapor pressure thus distilling water from a substance with a high vapor pressure to that of a low vapor pressure namely the phosphorous pentoxide. The gel was suspended in a three liter round bottom single necked flask fitted with a rubber stopper. Through the rubber stopper pertruded a stopcock, thermocouple and two lead wires for the heating element wound around the container for the gel. The thermocouple was placed at the very surface of the gel (2 g.). The phosphorous pentoxide was placed at the bottom of the flask. The entire flask was then submerged in a 25°C. constant water bath ± .005°C. The gel prepared in this manner was tested for known metallic elements by a medium quartz spectograph with results which showed it remarkably free from mettalic impurities.

In the third method vacuum technique was followed in that the gel was heated at a final pressure of .0001 mm. of mercury and then sealed off. This procedure required a longer time than either of the other two methods and gave results in agreement with those obtained with the gel prepared over phosphorous pentoxide.

Heat Measurements.- The gel, sealed in evacuated bulbs 2.5-3.0 cm. in diameter, of known water content, was placed in the cradle prepared for it and immersed in the water of the calorimeter. A volume of 125 ml. of water was used for the determinations. The Beckmann thermometer, stirrer, heating elements and thermopile were also entered in the 125 ml. of water. The assembly was then ready to be brought to equilibrium temperature with the copper sulfate bath, around the outer container of the silvered cup, and the temperature of the air bath in which the entire apparatus was held. This equilibrium stage required from four to six hours. It was best to begin all measurements at 25°C. instead of attempting to end at an equilibrium stage at that temperature. The reason obviously was associated with possibilities of heat exchanges. It was found that the heat transfer from the silvered cup to the outside was very small due to the air insulation surrounding the cup if the copper sulfate bath was held to within .05°C. of the temperature of the silvered cup. Care was always taken to be sure no heat entered the system from an outside source. The two Beckmann thermometers and thermopile gave two checks on the variations of temperature between the inner calorimeter and copper sulfate bath.

The small metallic stirrer rotating at about 100 r.p.m. gave no measureable heat of stirring. As a preliminary test of the assembled calorimeter a heat equivalent was taken and

then the whole again returned to 25°C. to come to equilibrium for the gel run. When equilibrium at 25°C. had resulted the bulb was broken at its tip by the screw and usually the bulb was completely shattered throwing the gel freely into the water. The rise in temperature of the inner calorimeter was followed with the same increase in temperature of the copper sulfate bath. The entire apparatus was then cooled to 25°C. until equilibrium became evident which required one to two hours. The heat equivalent was then determined and the average of four trials recorded.

The electrical energy used for determining the heat equivalent was evaluated by measuring the voltage drop across the heavy copper conductors leading to the heating element also measuring the voltage drop accross a standard resistance. Between one and ten readings for each of these voltage drops were made during a run and the average taken for calculations. The most constant source of current used was that obtained from two 6 v. storage batteries connected in parallel. Before using the current the batteries were discharged at a like rate for ten to thirty minutes or until constant voltage readings across a known resistance were obtained. After fully charging it was found expedient to discharge the parallel batteries at .1 amp for ten to twelve hours, thus hastening their equilibrium discharging condition.

The heat equivalent was calculated according to $H(\text{calories}) = I^2Rt/4.18$ or $EIt/4.18$. The temperature rise

of the electrical heat equivalent was an exact reproduction of the temperature rise of .500 to .005°C. caused by the gel.

Discussion.- According to Adams (Physics and Chemistry of Surfaces p. 200) the heat or energy liberated by wetting a silica gel surface is due to a destruction of total surface energy. The equation $U = W_{sl} - T \frac{dW_{sl}}{dT}$ shows that this total surface energy is composed of free surface energy and latent energy of the surface molecules themselves. U is total energy, W_{sl} is the work of adhesion or free energy of wetting, T is absolute temperature, and $T \frac{dW_{sl}}{dT}$ is a heat term or potential energy associated with the surface molecules. Available data indicates that most of the energy liberated by wetting must be due to the latter term. This would indicate that activated silica gel with its enormous area and honeycombed shell presents a surface of silica molecules which have tremendous potential energy.

Zsigmondy, van Bemmelen, and Anderson worked on the static control of water on fresh silica gel by means of sulfuric acid but evidently, working in the presence of air, they did not allow ample time for the adsorption to reach equilibrium for they found a decided hysteresis during the adsorption-desorption runs. In our data no noticeable hysteresis was observed unless its magnitude was below .001 g. in 2.500 g. At times the gel required a longer interval to attain equilibrium.

Table I

Acid % by wt.	X/M at Temperatures			
	15	25	40	60°C
96.7	.047	.046	.046	.046
91.4	.048	.048	.047	.047
85.6	.050	.049	.048	.048
78.2	.056	.055	.054	.053
71.2	.070	.068	.067	.065
61.9	.108	.105	.101	.099
53.1	.174	.170	.162	.156
44.4	.251	.242	.234	.225
32.8	.335	.331	.322	.316
19.0	.349	.347	.342	.335
00.0	.362	.358	.351	.341

Table I gives the results of equilibrating silica gel over sulfuric acid solutions at 15, 25, 40 and 60°C. The curves of fig. I follow the same general shape for each isotherm and indicate a dropping off of adsorption capacity at higher temperatures. If the vapor pressure vs % weight acid curve at 25°C. is compared to the above curve of the same temperature the two show great similarity in structure and forecast the shape of the vapor pressure - X/M curve.

Plotting the X/M values against vapor pressure (International Critical Tables, 3, 303) values at 25°C. gives a straight line graph (fig.2) which could indicate that as Rideal (Surface Chemistry, p. 58) has stated, "The transition from a

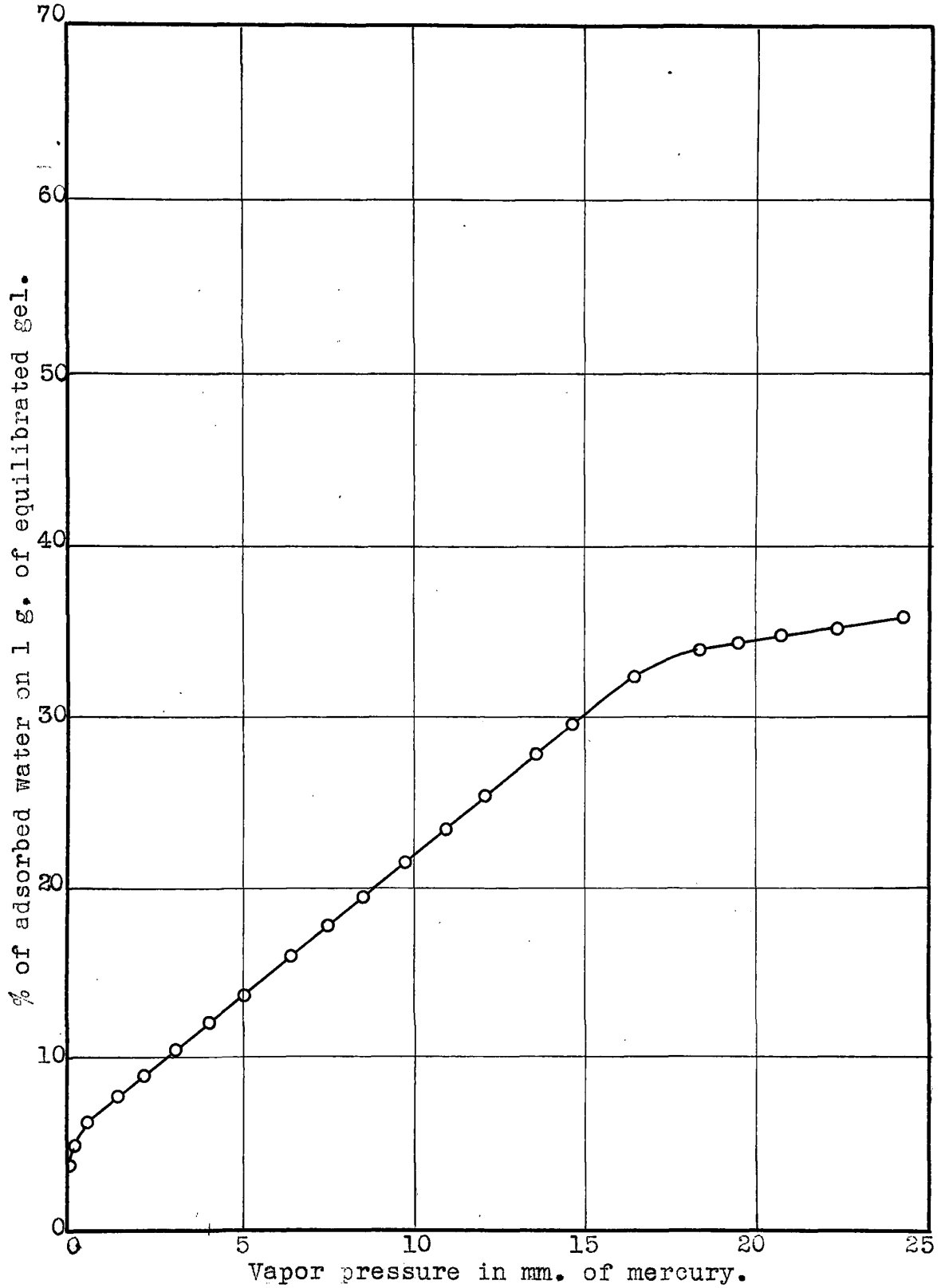

Fig. 2.- Adsorption of water vapor by silica gel at 25°C.

monomolecular layer to a polymolecular adsorbed layer, in such a bulk that its free surface would possess the free surface of the liquid in bulk, is not abrupt." Changing fig. 2 into a log-log curve (fig. 3) according to Freundlich's coordinates gives a curve with three straight sections to which reference will be made later.

In testing the applicability of Freundlich's, Patrick's and Gregg's Adsorption Equations we will observe only the central straight line section of the log-log graph of the X/M - vapor pressure curves at the various temperatures. Figs. 4, 5, and 6 give the general shape of the curves and Table II the slopes and constants of the lines. The variations

Table II

	Freundlich's		Patrick's		Gregg's	
	1/n	k	1/n	k	1/n	$k*10^{-4}$
15°	.707	70.66	.744	18.2	.763	30.2
25°	.767	38.23	.772	16.1		
40°	.825	15.85	.816	13.6		
60°	.898	4.74	.880	10.6	.882	21.3

over the temperature range in these figures are less in Patrick's and Gregg's than in Freundlich's with the added result that Patrick's, as Gregg's log-log isotherm curves all fall very close together. As long as Patrick's and Gregg's Adsorption Equations, however, do not give as they

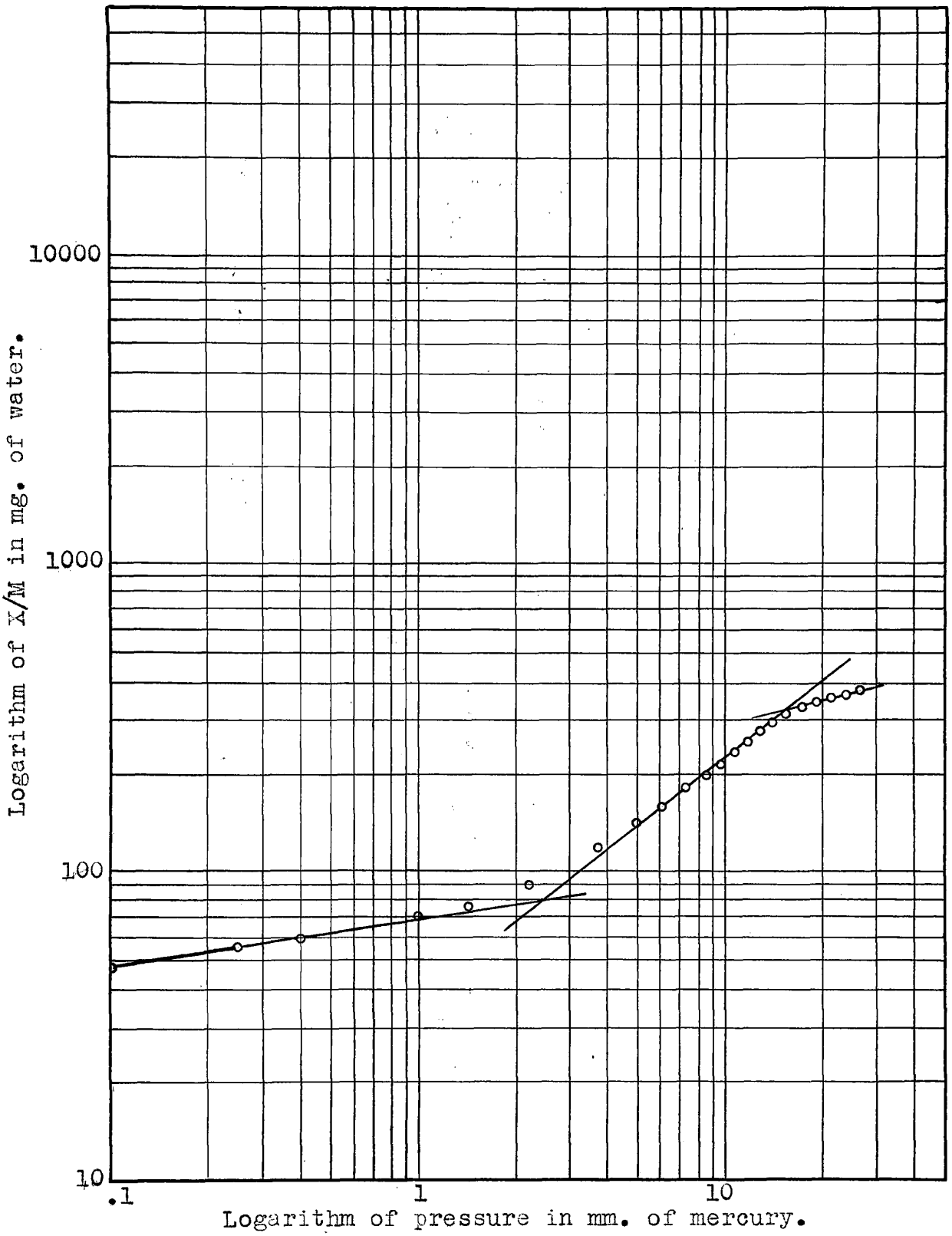

Fig. 3.- Freundlich's adsorption isotherm at 25°C.

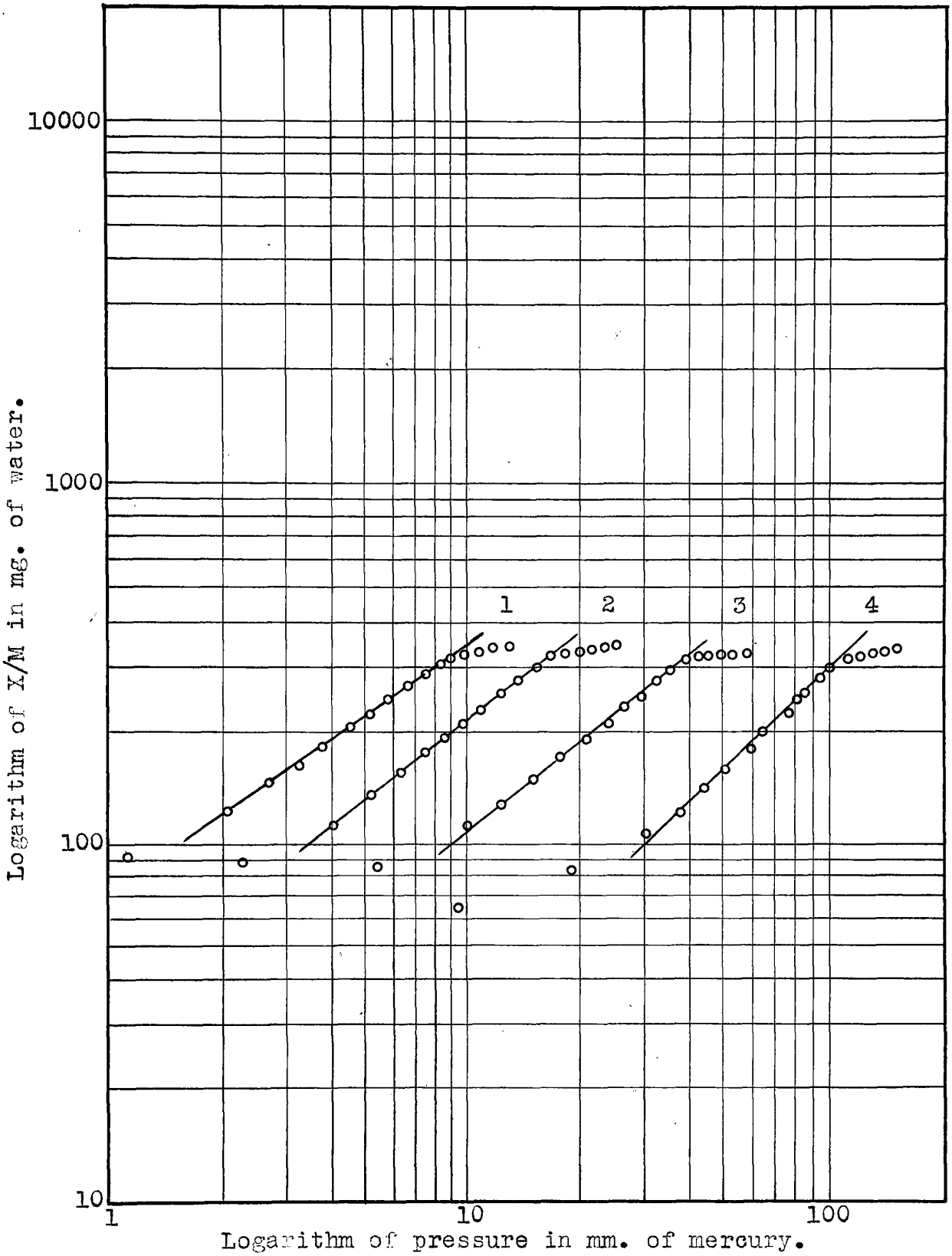

Fig. 4.- Freundlich's adsorption isotherms: No. 1, 15°C.; No. 2, 25°C.; No. 3, 40°C.; No. 4, 60°C.

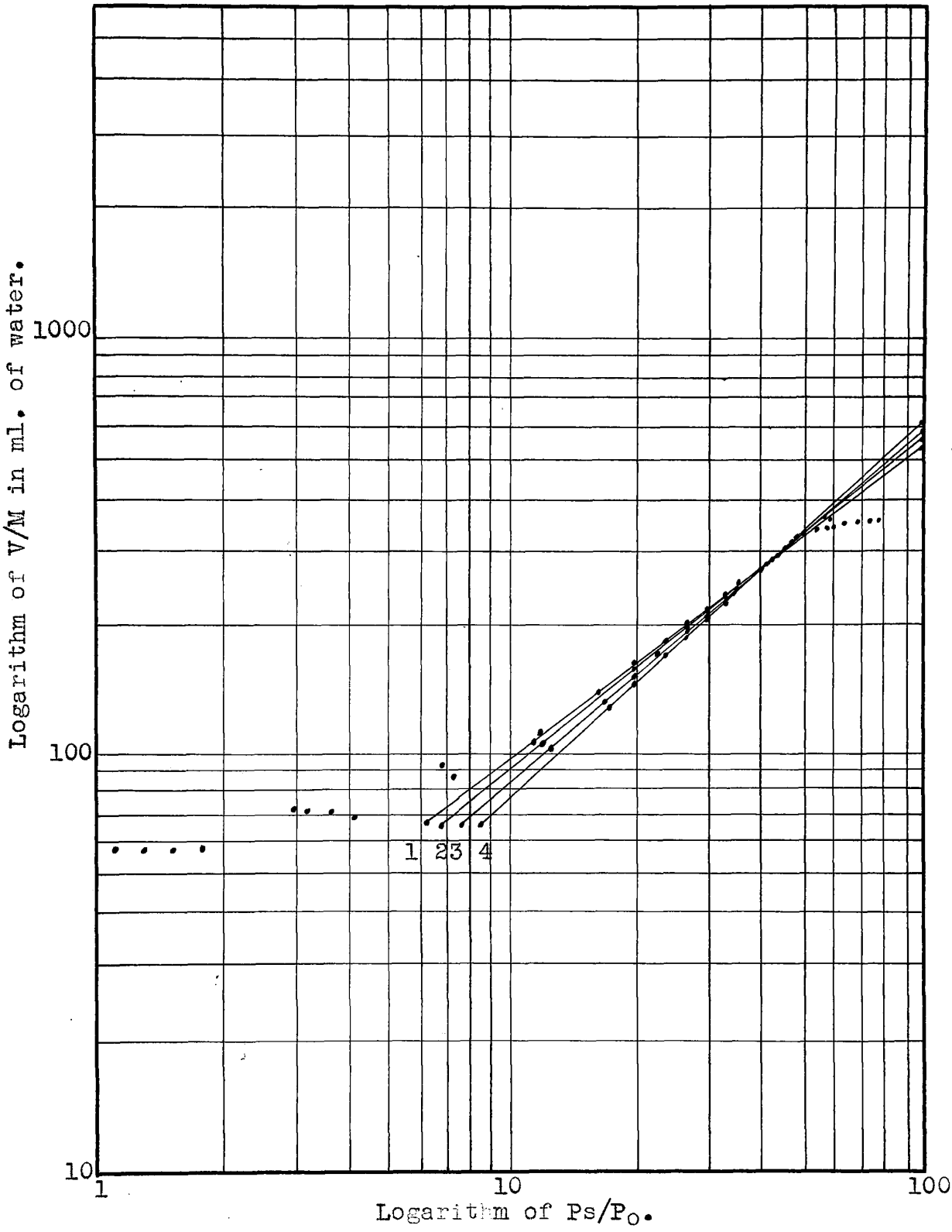

Fig. 5.- Patrick's adsorption isotherms: No. 1, 15°C.; No. 2, 25°C.; No. 3, 40°C.; No. 4, 60°C.

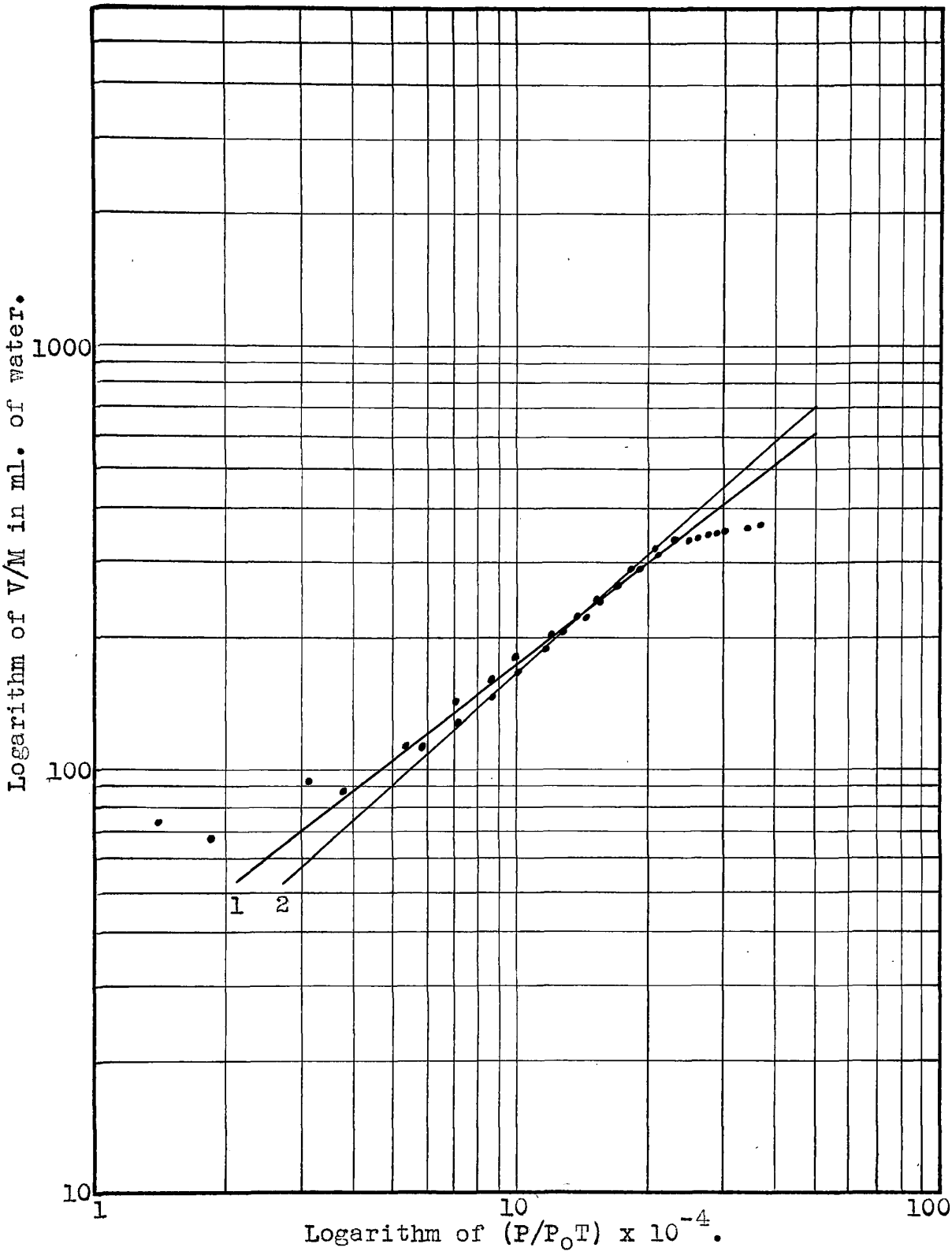

Fig. 6.- Gregg's adsorption isotherms:
No. 1, 15°C.; No. 2, 60°C.

were intended a means of calculating adsorption values at one temperature knowing them at another, we will deal only with Freundlich's simple relationship.

Curves from figs. 7, 7a and 7b are results paralleling parts of the experiments of Bartell and Almy (J.Phys.Chem., 36, 475 (1932)). The curves of fig. 7 are quite identical with their % water vs T°C. of activation curve. In both figs. 7a and 7b the activation temperature was 260°C. and although Bartell and Almy did not work at that temperature their results still indicate a difference which might be explained by noting that they worked with gels containing less than 4% water which is our value for gel of greatest activity. Obviously therefore their results are reasonable for they are probably only removing adsorbed gases and some adsorbed water in the 30 minutes of heating at 300°C. without destroying any of the internal surface by this short activation treatment. A longer heating period or higher temperature would result in a liberation of sufficient water to cause loss of activity. Due to the unreversibility of the activity of the gel containing less than 4% water Bartell and Almy's results cannot be expected to be exactly parallel to this work. For maximum activity they concluded that 300°C. for 30 minutes was best while we found 275°C. for many hours gave a gel of highest activity. They also state that water content of a gel is intimately connected with activity which agrees with our results but do not seem to place as much importance on the

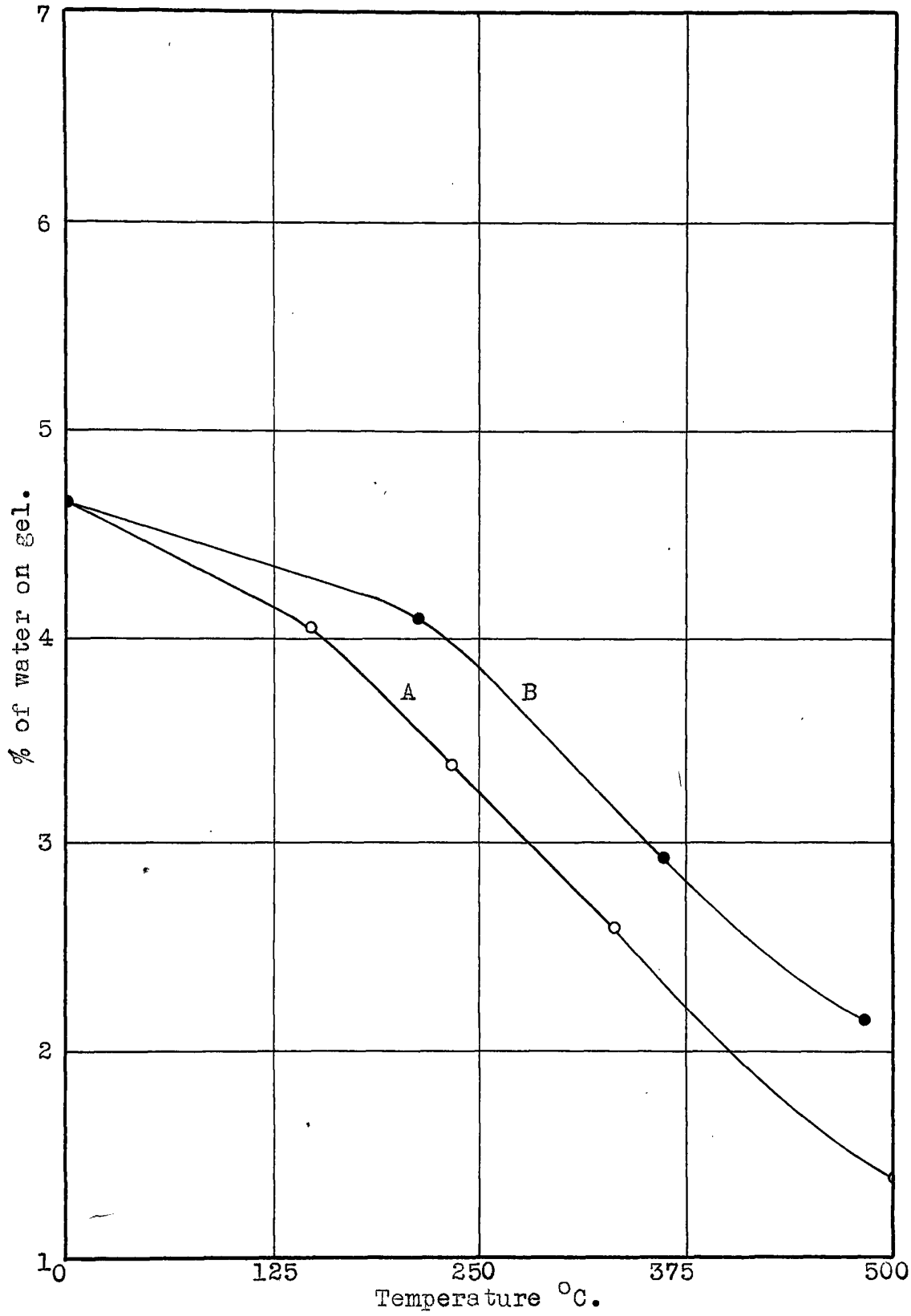

Fig. 7.- Relation of water content to temperature of activation: A, heating over P_2O_5; B, heating and evacuating.

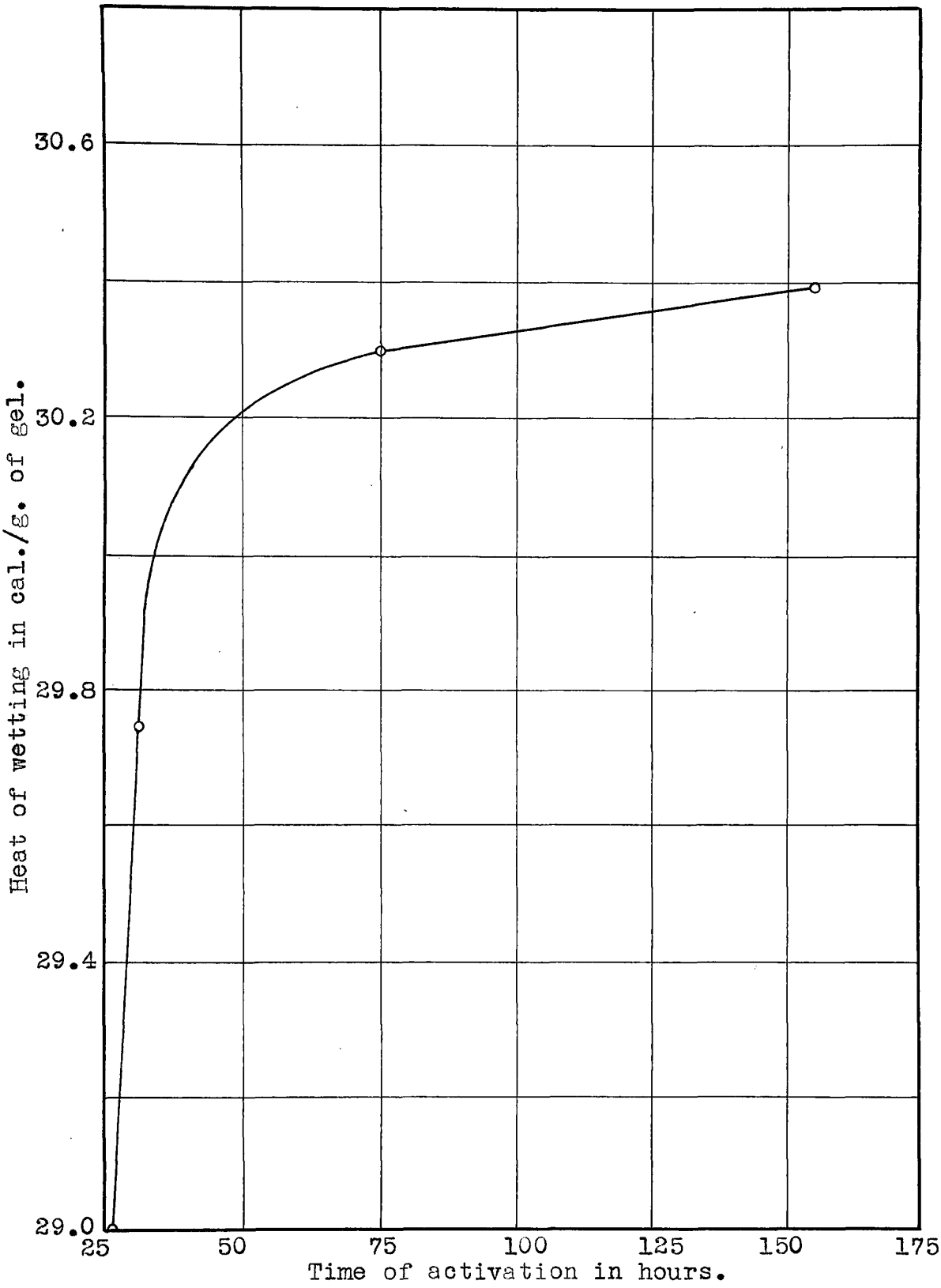

Fig. 7a.- Relation of heat of wetting to time of activation.

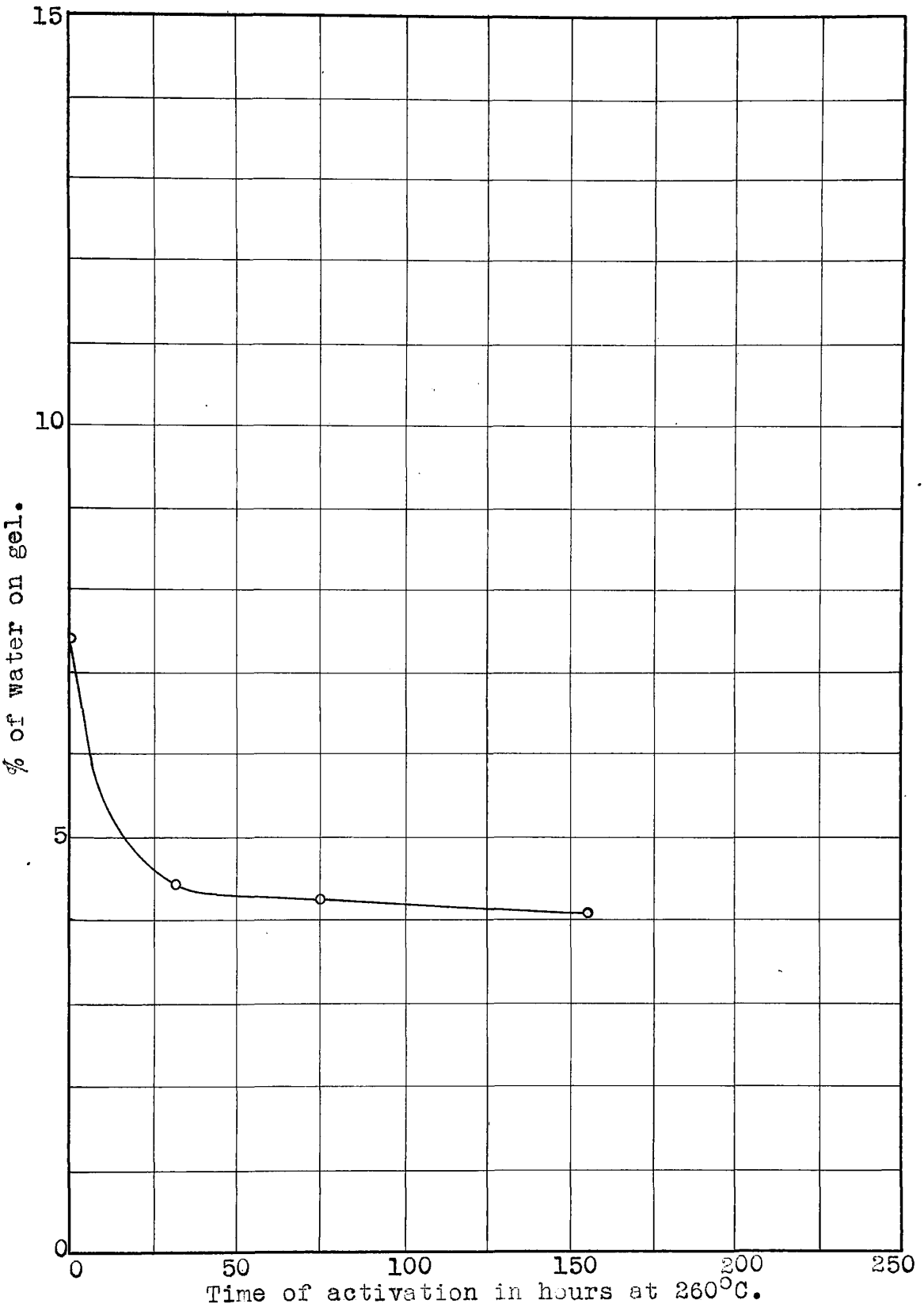

Fig. 7b.- The relation of water content to time of activation.

activation treatment.

In covering the range of water content of the gel from 0% to 36%, by weight, commercial concentrated sulfuric acid would prepare a gel only as low as 4.7% water content. To go still further the small vacuum electric furnace was constructed which produced the series of gels from 4.7% down to 1.4% water content. Taking 4.7% gel or gel equilibrated over concentrated sulfuric acid and heating it gradually from 25 to 500°C. produced the curve "A" of fig. 7. The noticeable fact, as indicated by this curve and later in the heat of wetting measurements, is that a change of condition of the water on the gel occurs at a water content of 4%. A water content below the 4% point produced a gel of lower activity as will be explained later.

The transition of color which accompanied the removal of water was interesting. With the application of heat the gel became colored ranging from light tan to almost black. The darkest color occurred during the preparation of the 4% water content gel and that gel of lower water content. The color did not in all cases indicate a more active gel although when colored the gel was very active as measured by heat of wetting. Another observance was that if the gel remained at the same temperature long enough the color would disappear, leaving at that time a gel which was the most active at that particular temperature and water content.

A longer time was necessary for fading of the color at the lower temperatures. This color change could be due to an unsaturation of molecular forces (Gilbert N. Lewis, J. Am. Chem. Soc., 38, 784 (1916)), a difference of refractive index (no water present on some surfaces), or a light interference phenomenon due to a condition of the inner surfaces with respect to each other. Whatever condition does exist it is readjusted by continual application of heat. If sealed in a vacuum bulb while colored the color will remain for years, if no heat is applied beyond room temperature, without loss of activity.

On the theory that the heat of wetting value will give an accurate means of evaluating activity determinations of the heat evolved from wetting gels of different water content from 1.4% to 35.8% have been made. Fig. 8 and table III give the actual experimental values obtained at 25°C.

Table III

% Water on Gel	Cal./g. Gel	% Water on Gel	Cal./g. Gel
35.80	0.10 (.02)	7.10	23.50 (.20)
34.60	0.20 (.04)	5.35	26.50 (.20)
28.50	2.25 (.05)	4.70	28.00 (.20)
25.50	3.75 (.05)	4.40	28.80 (.20)
24.75	4.25 (.05)	4.18	30.00 (.20)
20.35	7.50 (.06)	4.00	30.50*
		4.00	31.40*
19.90	7.80 (.06)	4.00	31.80*
17.10	10.30 (.10)	3.50	29.10 (.20)
12.70	15.25 (.05)	2.98	28.90 (.10)
12.05	16.10 (.05)	2.12	27.10 (.10)
7.50	22.80 (.20)	1.90	26.55 (.10)
		1.53	25.30 (.05)
		1.42	24.50 (.05)
		0.00	00.00

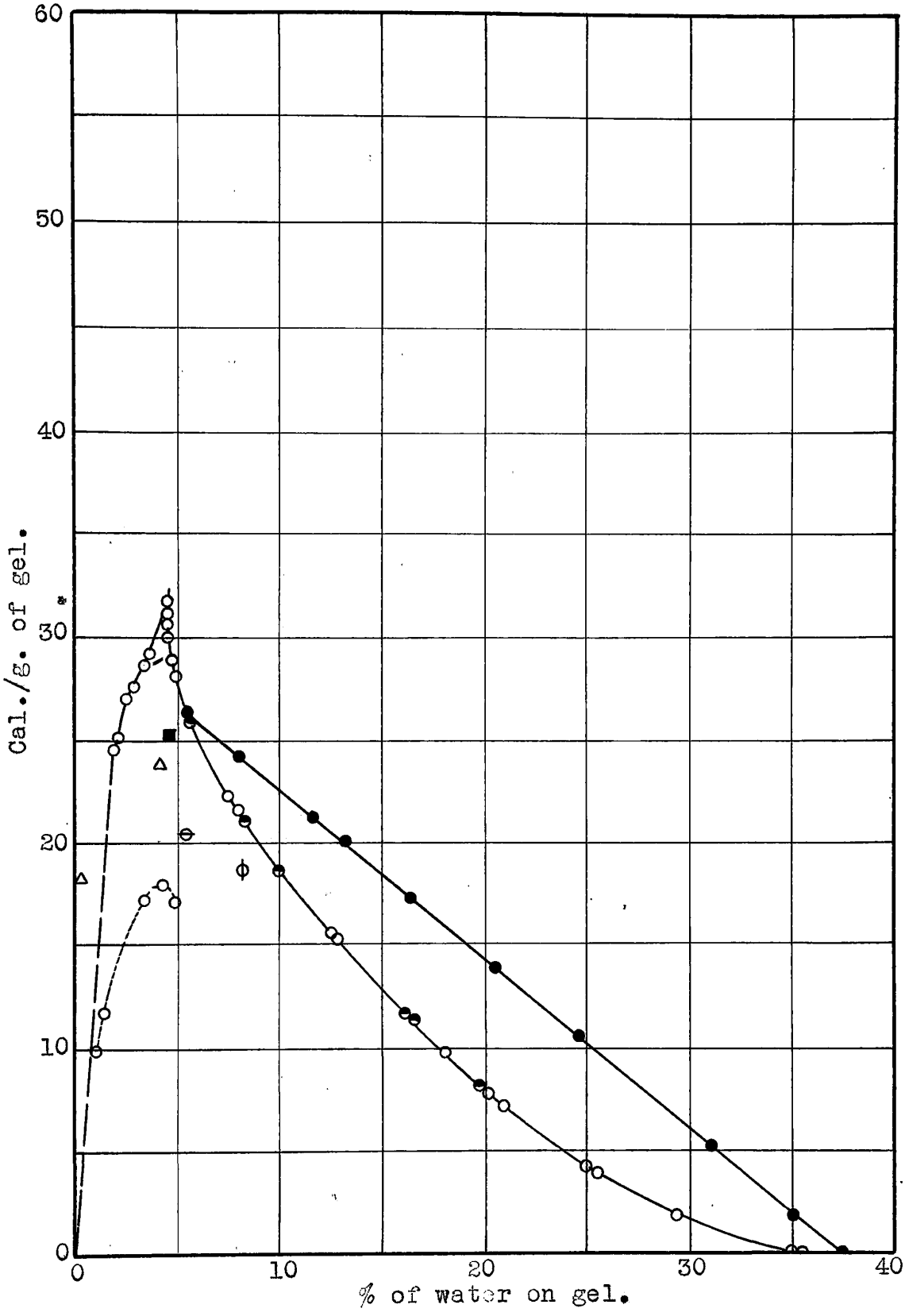

Fig. 8.- Heats of wetting of water on silica gel:
●, Ray and Ganguly, -o- Bartell and Almy;
⊖, Patrick and Greider; △ Bartell and Fu;
ϕ, Patrick and Grimm; ■ Stenzel; ● Nasif;
o, Ewing and Bauer.

The values are the mean from at least six trials with the maximum deviations in brackets. In the region of greatest activity the values obtained were variant due to a possibility that in this highly active condition small changes in the gel structure and manner of activation will cause a great difference in activity. The point "32 calories" is an interpolated one for values above 30 calories were difficult to duplicate. Below 4% water content the gel activity was reduced probably by destruction of its interior active surface, while for 0% water (fused gel) the particles seemed to be negative to wetting although the transparent particles were wetted.

Referring to fig. 8 that portion of the curve on the right side of the 4% gel was a perfectly reversible procedure but that portion of the curve on the left of the most active point, 4%, was not reversible. That is, once the gel had been activated to a water content of less than 4%, the high activity of 32 cal./ g. of gel could not again be reached. In other words, once the water below 4% had been removed it could not be replaced on the gel with a corresponding increase of activity to 32 cal./g of gel resulting.

Fitting the equation of a circle to the experimental points of the curve of fig. 8 the extended line crosses the % water axis at 37.7% which will be taken as the total amount of water fillable space of the silica gel. Ray and Ganguly

gave 37.5% water content as the saturation limit for their gel. In an earlier experiment by Ikerman (unpublished) conducted in this laboratory on this gel a volume of .333 c.c. was determined as the volume of water taken on at saturation. If we subtract from .377 (considering the total water on the gel as averaging a density value of 1.00) the value of .040 giving .337 c.c., then our value for the volume of water on the gel at saturation compares favorably with the former value of .333 c.c.

The heat of wetting of silica gel of varying amounts of water have been evaluated by Patrick, Ray and Ganguly, Patrick and Grimm, Patrick and Greider, Bartell and Almy, and Bartell and Fu with values ranging from 19 to 26 cal./g. for their most active gel. The values for the heat of wetting by these authors are also given on fig. 8 as accurately as their water contents will permit. With these various values indicating either a difference in water content of gel, activation, or gel structure investigators are quite evident to differ in results obtained unless a knowledge of the entire history of each gel sample indicating paralleling work is sufficient proof of the duplicability of results.

Bartell and Fu (Colloid Sym. Mono., 7,135 (1929)) have calculated the specific surface of silica from adhesion tension data using an equation of the Gibbs Hemholtz type and obtained a value of 4.5×10^6 cm^2. They used for their value of change of latent energy of the molecules -.1511

ergs/cm^2 which is the value for water therefore neglecting the potential energy associated with the silica surface molecules. They also obtained a value of 24.31 cal./ g. of hydrated (4% water content) silica for the heat of wetting of water and assumed that the surface exposed was predominately silica molecules creating an area of 7.5 x 10^6 cm^2 calculated by the equation employed by Patrick and Grimm. Also, Bartell and Fu from an equation similar to one presented by Harkins and Ewing and from interfacial tension data calculated an area of 4.5 x 10^6 cm^2 for a dehydrated gel. This value of 24.31 cal./g. of gel is distinctly above that obtained by Bartell and Almy but the activation history of the three types of gels is also different as is their water content. A gel from the data of Bartell and Fu with a water content of 4% develops the highest heat of wetting which indicates that their gel also has a high activity point at 4% water content.

Fig. 9 is an attempt to compare our heats of wetting values with the net heats of adsorption of other investigators. The results of the experiments of Lamb and Coolidge agreed with their empirical equation and fig. 10 indicates that heat of wetting values will also determine a straight line except for the most active gel. The total heat of adsorption in this case was determined from table IV where the change in cal./g. of gel for .01 g. of water from 4% to 37.7% is tabulated.

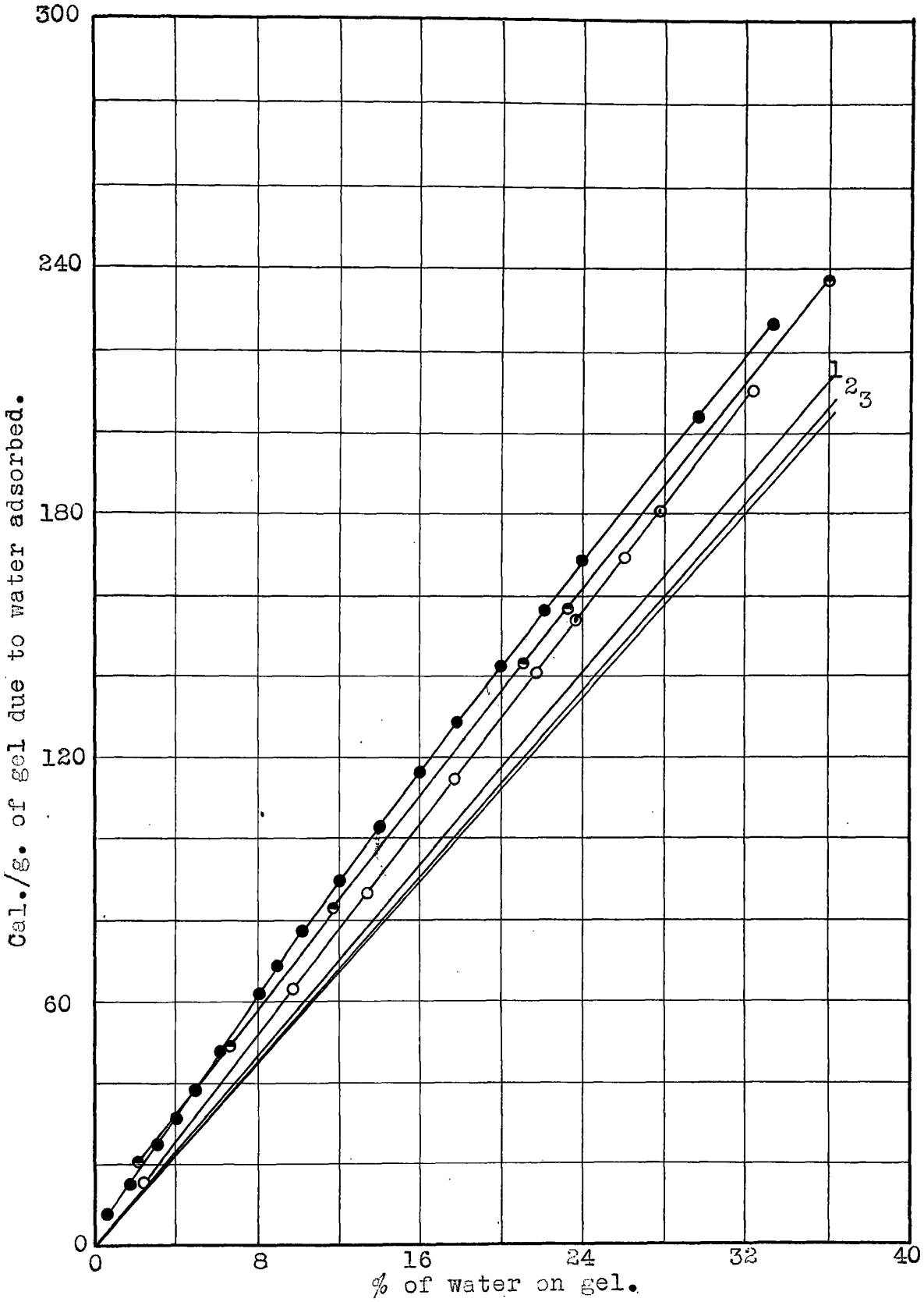

Fig. 9.- Heat of adsorption of water vapor on silica gel: ○, Ray and Ganguly; ◐, Patrick and Greider; ●, Ewing and Bauer. Nos. 1, 2 and 3 are the heats of condensation of water vapor at 0°C., 25°C. and 30°C. respectively.

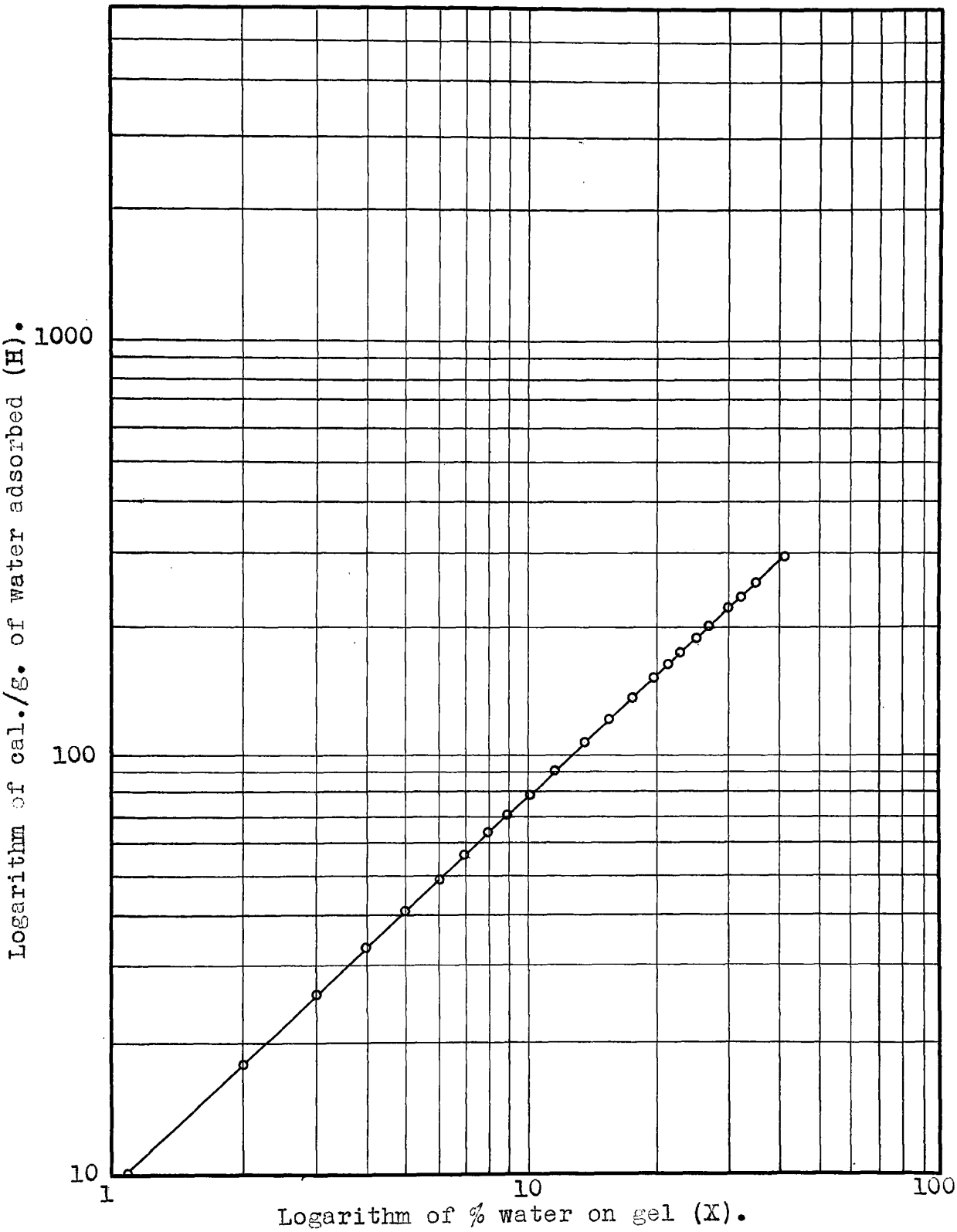

Fig. 10.- Application of the Lamb and Coolidge Empirical Equation of $H = mX^n$; m is 9.74 and n is .898.

Table IV

% Water on Gel	Cal./g. Gel	-d Cal.	Ave. /.01g. Water	Diff.
4%	32.00			
5	27.25	4.75		
6	25.25	2.00		
7	23.60	1.65		
8	22.00	1.60	2.50	
9	20.50	1.50		
10	19.00	1.50		1.04
11	17.60	1.40		
12	16.15	1.45	1.46	
13	14.90	1.30		
14	13.65	1.25		.26
15	12.50	1.15		
16	11.45	1.05	1.20	
17	10.40	1.05		
18	9.45	.95		.26
19	8.60	.85		
20	7.70	.90	.94	
21	6.90	.80		
22	6.15	.75		.19
23	5.40	.75		
24	4.70	.70	.75	
25	4.10	.60		
26	3.50	.60		.20
27	2.95	.55		
28	2.50	.45	.55	
29	2.05	.45		
30	1.60	.45		.15
31	1.20	.40		
32	.90	.30	.40	
33	.60	.30		
34	.35	.25		
35	.15	.20		
37.7	0.00	.15		

Adding the heat of condensation of the total number of .01 g. of water to the total change in cal./g. of gel caused by this amount of water starting at 4% gel and 32 cal./g. of gel will give the total heat of adsorption.

In fig. 11 an attempt is made to apply an equation to the heat of wetting data in order to be able to determine the heat of wetting obtainable from a gel of known water content, with reference to the gel used in this experiment. The graph is semi log with the cal./ g. of gel as the unit scale and the % water content of the gel as the log scale. The central portion falls on a decidedly straight line but the extremities deviate from the equation given directly beneath the figure, and one of the deviations is at a water content of 8%.

In an experiment on determination of adsorbed water density of varying amounts of water, Ewing and Spurway (j.Am.Chem.Soc.,52, 4635 (1930)) indicated a break in the % water adsorbed vs. density curve at a water content of approximately 8% which agrees with our first discontinuity in figs. 3 and 11. In their data the break comes at the 4% point but in the preparation of their gel 4% water was with the gel before the addition of their first 4% water.

It is noteworthy that the simple relationships observed by Ray and Ganguly as to the ratio of mols of water to mols of silica were observed in these results. At the point of greatest activity (4% gel) the ratio is 2 mols of water to 15 mols of silica while at the saturation point the ratio becomes 30 mols of water to 15 mols of silica.

In order to explain the heat effect observed upon

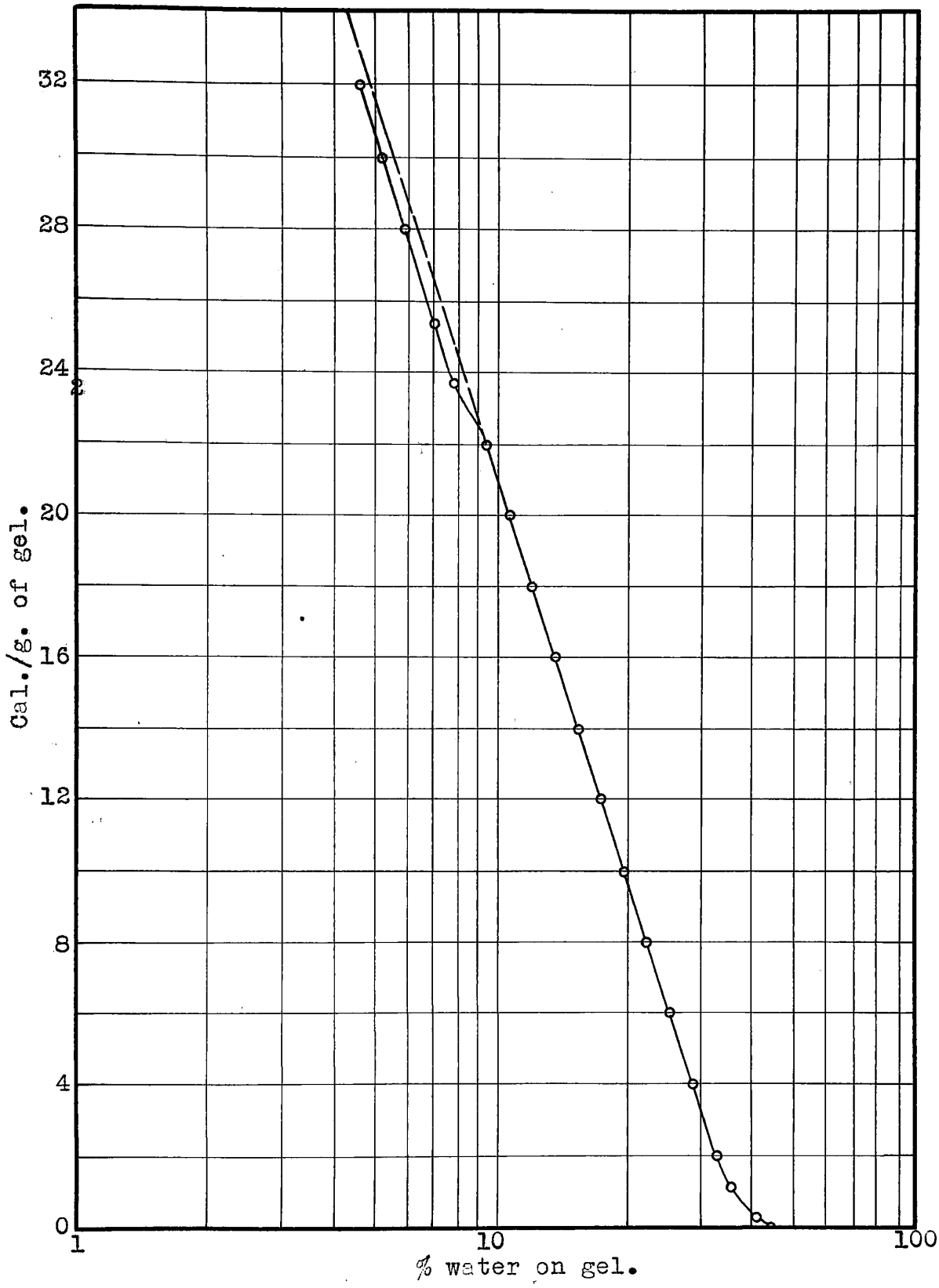

Fig. 11.- Heat evolved by gel of definite water content.
An equation for the line is h = m log X/M + K
where m is -34.7 and K is 88.071.

immersing a gel in water as due to destruction of a surface its area must be evaluated. As the areas calculated for silica gel or silca have varied from 4.5×10^6 cm.^{2} to 13×10^6 cm.^{2} depending on the theory, method, liquid for wetting or condition of gel used and also the accuracy we will refer to figs. 3 and 11 for data on which to base our assumptions for area. The straight lines drawn through the three straight portions of fig. 3 indicate a change in the gel condition or gel water condition. Likewise the curve of fig. 11 shows two changes in activity at approximately the same points that were indicated in fig. 3. The first point, that of gel of 8% water content, will serve as evidence to assume that when gel has 8% water on it that the surface of the gel is covered by a monomolecular layer of water molecules. In this assumption Langmuir's theory of monomolecular adsorption over a plain surface is accepted and a further assumption that the gel will in part exhibit such a plain surface. Areas covered by a given amount of water are calculated from "n" equals 6.06×10^{23}, Langmuir's value for the area covered by one molecule of water of 7.4×10^{-16} cm.^{2}, and that the adsorbed water has a density of liquid water. If 4% water is the lowest value before the gel begins to lose its activity this might indicate that the first 4% water is an integral part of the silica gel. Then the next 4% water is that water covering the silica gel surface with a monomolecular

layer, when calculated this area becomes 1 x 10^6cm.^{2}, Patrick has stated that the internal area is much less than 6 x 10^6cm.^{2} and that the initial stages of adsorption of water consist of the formation of a monomolecular layer over the surface.

Table IV lists the - cal./ g. of gel/ .01 g. of water adsorbed by the gel. In this data, taken from fig. 8, are grouped the above values and with their averages per .01 g. of water for changes of .04 g. of water adsorbed. The differences between the averages is greatest between the first and second groupings while the averages for the next four groupings and the second group decrease in quite regular value.

Another assumption must be made to account for the enormous energy liberated from such a small area namely, that the surface of the gel is dry at the 4% point and that to destroy the total energy associated with the surface by wetting with water is the seat of most of the energy. To completely wet a surface, so that further water will only destroy a water surface, requires at least five or six layers of water molecules. Selecting six as the number of layers, the weight of water per gram of gel needed will be .24 g. Increasing by .04 g. and the end of the second straight portion of the curves of fig. 3 and fig. 11 is reached at .28 g. or 28% water. The curves seem to indicate the

break at .32 g. but a statement later will explain the reason for the previous decision.

In the equation $u = W_{sl}A - T(dW_{sl}/dT)A$, where "A" is the area, we are given the value of 155.6 ergs/ cm.^{2} for the adhesion tension of water against silica but are not given the factor dW_{sl}/dT. As long as "u" is obtained experimentally and "A" by assumption dW_{sl}/dT can be calculated becoming approximately equal to -4.00 ergs/cm.^{2}. This would indicate the high activity or potential energy of the surface molecules that was predicted earlier. To determine the heat evolved when a water surface is destroyed involves only the total surface energy of a bulk liquid of water:

$u = (72.8 \times 1 \times 10^6 + 298 \times 4 \times 1 \times 10^6) / 4.185 \times 10^7 =$

2.8 cal.

Returning to figs. 3 and 11 a break in the curves is noted at approximately this point which might indicate a saturation of the silica surface and destruction of only water surface from there on to complete submersion in water. An interesting experimental observation is that gel equilibrated in an atmosphere saturated with water vapor will still exhibit a heat of wetting when immersed in water liquid. This indication of capillary condensation amounts to 28% to 35.8% water content. Assuming that the total surface is covered by a layer of molecules six deep and that capillaries present at the beginnins will be so nearly filled by these layers of water that a distinct depression of the vapor

pressure results until at the point 35.8% the capillaries are filled and the entire surface presents at this point a total surface of water identical with bulk water. At this point and temperature a state of equilibrium will exist between evaporation and condensation so that the total weight of water on the gel will not increase. This condition will exist with water vapor until water liquid reduces the remaining semi-capillary spaces by flowing into them. The net heat of adsorption of a gas or vapor on silica gel will always be slightly lower than the heat of wetting.

Summary

1. An adsorption-desorption curve of water vapor on silica gel showing no hysteresis was obtained.

2. Adsorption isotherm equations were applied to the above results.

3. The activity was evaluated for gels of varying water content as heat of wetting measurements.

4. A maximum in the heat of wetting determinations at a water content of 4% for this particular silica gel was observed.

5. The activation of the gel must be carried out carefully so that the water on the gel is evenly distributed over the surface or at least is in a state of equilibrium with the gel surface.

6. An area of 1×10^6 cm.^{2} is postulated as the total wettable surface of this silica gel.

7. There is an indication that the first water on the gel is monomolecular, the next as a polymolecular (five to six) layer, and the final as water condensed in the remaining portion of the capillaries.

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